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Sulphate Adsorption in Soils of North and Northeast Iran

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Abstract: Gypsum ($CaSO_4 \cdot 2H_2O$) is used in agriculture both as a source of calcium (Ca) and sulphate (SO_4^{2-}) and as an amendment to improve soil structure. The effect of gypsum on the adsorption of SO_4^{2-} in irrigated and nonirrigated soils was examined. Almost all of the indigenous sulphate (SO_4) in a range of Golesthan and North Khorasan soils with moderate pH values (>6) was found to be present in the soil solution and, as a consequence, was highly susceptible to leaching. The adsorption of sulphate to the soils receiving no gypsum was greater with correlation coefficient of $r = 0.91$ at $0 \, kg \, S \, ha^{-1}$ as compared to the soils received $40 \, kg \, ha^{-1}$ of gypsum as fertilizer with the value of $r = 0.88$ in Golesthan Province. The same trend was observed in Khorasan Province with $r = 0.79$ and $r = 0.75$ with soils receiving 0 and $40 \, kg \, S \, ha^{-1}$, respectively. The results were more pronounced in irrigated fields for both provinces. The amount of sulphate adsorption in Golesthan Province soils was comparatively greater than soils of Khorasan Province. The results raise questions regarding the efficiency of SO^4-containing fertilizers in correcting and preventing S deficiency in situations where leaching is a concern.

Keywords: Adsorption, Golestan, irrigated soil, Khorasan, sulphate

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INTRODUCTION

Crop deficiencies of sulphur (S) have been appearing worldwide with increasing frequency, particularly in the past decade (Morris and Shin 1988). Factors that have been implicated include decreased inputs of S, due to a decline in deposition of atmospheric S (Bristow and Garwood 1984) and the replacement of S-containing fertilizer by high-analysis materials containing small or insignificant amounts of S. Concurrent with the decline in S inputs, the requirement for S has been increasing because of improved crop yield brought about, in part, by heavier use of fertilizer nitrogen. In north and northeast Iran, the crop responses to S have been reported in Golesthan and Khorasan Provinces with low S inputs (Shahsavani 2002). Adsorption by particulate matter influences the solution concentration and transport rate of sulphate (Bolan et al. 1987; Curtin and Syers 1990; McGrath and Zhao 1996; Kaparmwang, Esu, and Chude 1997). Thus, the capacity of a soil to sorb sulphate is an important factor that influences sulphate leaching and hence the availability of sulphate to plant. Soils vary in their sorption capacity for sulphate, and sulphate sorption is affected significantly by management practices, such as gypsum addition. Sulphate is sorbed by soils less strongly than phosphate (Hasan, Fox, and Boyd 1970; Haque and Wamsley 1973) and more strongly than nonspecifically sorbed anions, such as chloride (Hingston, Posner, and Quirk 1972).

The main purpose of this article is to report on studies carried out on a large group of soils, with contrasting physicochemical properties, to determine the extent of adsorption of added SO_4 and its relationship with soil properties. In this study, the effects of gypsum addition on the sorption of sulphate in a range of Golesthan and Khorasan soils are investigated.

MATERIALS AND METHODS

A field survey was carried out during April 1998 to establish the adsorption capacity of soil in two different climatic regions of Iran. The first region was Golestan Province in northern Iran; the second region was Khorasan Province in the northeast of Iran. These surveys were based on 60 field samplings, 30 samples from each province. In each province, 15 samples were from irrigated areas and 15 from nonirrigated areas on the basis of crop stand and visual appearance (from vigorous healthy-looking crops to very poor-looking crops). Samples of representative soil series were taken at 0–30- and 30–60-cm depths. Fifteen cores were taken from each depth in each field and bulked. Most parts of Golestan Province were covered in this survey. In case of Khorasan Province, only the northern part of this province was covered in this survey (Shahsavani et al. 2003).

Soil samples were air dried and passed through a 2-mm sieve for particle-size analysis using Day's method (Day 1965). Organic C was determined by

the Walkley–Black procedure utilizing $K_2Cr_2O_7$ and H_2SO_4 (Walkley and Black 1934). Soil pH was determined with a glass electrode at a soil–water ratio of 1:2 and with a digital pH meter. Electrical conductivity (EC) was determined using a digital electrical-conductivity meter. Active $CaCO_3$ was determined by Piper's method (Piper 1966). Mineralizable nitrogen (N) was estimated by an alkaline permanganate method (Subbiah and Asija 1956). Phosphorus (P) was extracted with sodium bicarbonate (Olsen et al. 1954). Their physicochemical characteristics and different forms of S are reported in Table 1.

Field experiments were established at four sites, irrigated and nonirrigated fields, to evaluate the sulphate adsorption to applied S fertilizer. In general, sites were selected on the basis of the 1998 survey of soil and plant S concentrations (Shahsavani et al. 2003). The soils were all medium coarse-textured soils (silty loam to sandy loam) containing small amounts of SO_4-S ($<10\,mg\,kg^{-1}$). Trial sites were divided into three blocks, and each block divided into four plots with each plot measuring $5 \times 10\,m$.

SO_4 was extracted with water (Massoumi and Cornfield 1963), 0.01 M $CaCl_2$ (Williams and Steinberg 1959), and 0.01 M $Ca(H_2PO_4)_2$ (Ensminger 1954) at a soil–extractant ratio of 1:5 and measured using the turbidimetric method (Massoumi and Cornfield 1963). Approximately 0.4 g of activated charcoal (SO_4^{-2}-free) was added to each tube to remove soluble organic compounds. After centrifugation (5000 rpm for 10 min) and filtration through Whatman No. 42 paper, SO_4 in solution was determined using the turbidimetric method.

Sulphate adsorption was determined from soils taken after harvesting the wheat crop in 1999 from two depths in soils of Golesthan and Khorasan Provinces. Sulphate adsorption was investigated in a system containing

Table 1. General properties of the soils from irrigated and rainfed fields of Golestan and Khorasan Provinces

Soil characteristics	Golestan Province		Khorasan Province	
	Irrigated	Rainfed	Irrigated	Rainfed
Texture	Silt loam	Loam	Silt loam	Sand loam
pH	8.2	8.3	8.1	8.5
EC (mS/cm)	0.19	0.21	0.23	0.33
Total N (%)	0.14	0.15	0.09	0.07
Available P (mg kg^{-1})	18.5	43.2	24.2	11.6
Total S (mg kg^{-1})	312	344	234	307
Water-extractable SO_4-S (mg kg^{-1})	8.50	3.70	2.00	1.30
$CaCl_2$-extractable SO_4-S (mg kg^{-1})	1.28	2.08	1.36	3.64
Phosphate-extractable SO_4-S (mg kg^{-1})	4.0	21.6	39.4	21.3
Biomass-S (mg kg^{-1})	10.5	8.60	11.0	8.80
Total S (mg kg^{-1})	276	205	252	173

different amounts of $CaSO_4$ and 0.01 M $CaCl_2$. Soil samples were equilibrated with $CaSO_4/CaCl_2$ solution (5 g soil: 40 mL solution in preweighed centrifuge tubes) in which the amount of SO_4 ranged from 0 to $30\,mg^{-1}$ for 16 h, after which the supernatant solutions were separated from the soil by centrifugation and filtration (Whatman No. 41 paper). The amounts of SO_4 retained by the soil were calculated from the decrease in concentration of SO_4 during equilibration. Centrifuge tubes were weighed to determined the entrapped solution, 0.01 M $CaCl_2$ was added by weight to 40 mL. It was shaken for 16 h and centrifuged, and the supernatant removed by filtration (Whatman No. 41 paper). The amount of desorbed SO_4 from the soil was calculated from the amount of SO_4 in solution after $CaCl_2$ addition minus the amount of SO_4 in solution before $CaCl_2$ addition. The amount of SO_4 in solution was measured by ion-exchange chromatography. Data analysis done with analysis of variance (ANOVA) was performed on all data sets to test the significance of the effect of S treatments at each site. Regression analyses of data were done where required. Statistical packages were used (MiniTab 12 and Microsoft Excel 1997).

RESULTS AND DISCUSSION

Changes in Soil Sulphate Level

The amounts of $CaCl_2$-extractable SO_4-S after harvest in spring 1999 ranged between 0.20 at S_0 to $3.66\,mg\,kg^{-1}$ at S_{40} in soils from 0–30 cm with irrigation and from 0.15 at S_0 to $4.85\,mg\,kg^{-1}$ at S_{40} in soils from 0–30 cm of nonirrigated fields (Table 2). Water-extractable SO_4-S level were higher in soils from the 30–60-cm depth compared to topsoil of both irrigated and nonirrigated fields. The amounts SO_4-S ranged from 2.34 at S_0 to $6.86\,mg\,kg^{-1}$ at S_{40} in the subsoil of irrigated field and from 2.86 at S_0 to $7.32\,mg\,kg^{-1}$ at S_{40} in subsoil of nonirrigated field (Table 2).

In the absence of applied S, the mean $Ca(H_2PO_4)_2$-extractable SO_4-S levels varied from 2.27 to $3.85\,mg\,kg^{-1}$ in soils from irrigated and nonirrigated fields.

The SO_4-S level in soils from 0–30- and 30–60-cm depths at the end of the growth period increased appreciably with increasing S application across all treatments. The SO_4-S level was higher in subsoils compared to top soils, and it varied between 2.27 and $4.98\,mg\,kg^{-1}$ in the topsoil and 3.65 and $7.21\,mg\,kg^{-1}$ in the subsoil (Table 2).

The concentration of $CaCl_2$-extractable SO_4-S in soils from irrigated and nonirrigated fields ranged between 1.64 at S_0 to 3.51 at S_{40} $mg\,kg^{-1}$ in soils from 0–30 cm of irrigated field and from 1.21 at S_0 to $3.72\,mg\,kg^{-1}$ in soils from 0–30 cm of nonirrigated field. The amounts of SO_4-S in the soil increased with spring S application across both irrigation treatments (Table 3). In the absence of applied S, the water-extractable SO_4-S levels

Table 2. Amounts of SO_4-S (mg kg^{-1}) extracted with 0.01 M $CaCl_2$, water, and $Ca(H_2PO_4)_2$-extractable SO_4-S from soils after harvest in Golestan Province (1999–2000)

| Applied gypsum (kg S ha^{-1}) | Irrigated | | | | | | Nonirrigated | | | | | |
| | $CaCl_2$ | | Water | | $Ca(H_2PO_4)_2$ | | $CaCl_2$ | | Water | | $Ca(H_2PO_4)_2$ | |
	0–30 cm	30–60 cm	0–30 cm	30–60 cm	0–30 cm	30–60 cm	0–30 cm	30–60 cm	0–30 cm	30–60 cm	0–30 cm	30–60 cm
0	0.20	2.21	1.53	2.34	2.27	3.65	0.15	1.86	1.78	2.86	2.35	3.85
20	2.88	3.75	3.84	4.52	3.56	5.68	3.21	5.23	3.46	5.65	3.86	6.11
40	3.66	5.86	5.36	6.86	4.98	6.88	4.85	7.65	5.23	7.32	4.23	7.21
Mean	2.25	3.94	3.57	4.57	3.60	5.47	2.85	4.91	3.49	5.27	3.48	5.72
SED	0.094	0.104	0.11	0.12	0.08	0.13	0.05	0.051	0.051	0.056	0.081	0.093
Sig	***	***	***	***	***	***	***	***	***	***	***	***1

NS = not significant.

∗ = p < 0.05.

∗∗ = p < 0.01.

∗∗∗ = p < 0.001.

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Table 3. Amounts of SO_4-S (mg kg^{-1}) extracted with 0.01 M $CaCl_2$, water, and $Ca(H_2PO_4)_2$-extractable SO_4-S from soils after harvest in Khorasan Province (1999–2000)

Applied gypsum (kg S ha^{-1})	Irrigated						Nonirrigated					
	$CaCl_2$		Water		$Ca(H_2PO_4)_2$		$CaCl_2$		Water		$Ca(H_2PO_4)_2$	
	0–30 cm	30–60 cm	0–30 cm	30–60 cm	0–30 cm	30–60 cm	0–30 cm	30–60 cm	0–30 cm	30–60 cm	0–30 cm	30–60 cm
0	1.64	1.45	1.06	3.31	2.31	3.56	1.21	1.43	1.08	4.41	2.64	3.81
20	2.38	2.89	2.81	4.38	3.61	4.28	2.87	3.21	3.81	5.61	3.83	5.21
40	3.51	3.91	3.98	5.21	4.28	5.69	3.72	3.95	4.93	6.26	5.21	6.89
Mean	2.51	2.75	2.61	4.30	3.40	4.51	2.60	2.86	2.94	5.43	3.89	5.97
SED	0.14	0.084	0.19	0.08	0.12	6.29	0.11	0.13	0.12	0.10	0.13	0.08
Sig	**	***	**	**	***	***	***	***	***	***	***	***

varied from 1.06 to 4.41 mg kg^{-1} in soils from irrigated and nonirrigated fields. Mean SO_4-S varied between 1.06 and 4.93 mg kg^{-1} in topsoil and 3.31 to 6.26 mg kg^{-1} in subsoils with and without irrigation (Table 3). Amounts of $Ca(H_2PO_4)_2$-extractable SO_4-S ranged from 2.31 at S_0 to 4.28 mg kg^{-1} at S_{40} in soils from 0–30 cm of irrigated fields and from 2.64 at S_0 to 5.21 mg kg^{-1} at S_{40} in soils from 0–30 cm of nonirrigated fields (Table 3).

Sulphate adsorption was determined from soils taken after harvesting the wheat crop in 1999 from two depths in plots receiving no S and from plots receiving 40 kg S ha^{-1}. Sulphate adsorption was low in all soils from irrigated and nonirrigated fields of Golestan Province and the amount of sulphate adsorbed at 20 mg L^{-1} was more in topsoil than subsoil. However, the values were higher in the plots receiving no S compared to the plots receiving 40 kg S ha^{-1}. This may be due to a lower concentration of SO_4-S in the surface layer and a greater tendency for the soil colloids to adsorb SO_4-S compared to plots that already received higher amounts of SO_4-S (Figure 1).

Sulphate adsorption was low in soils from both irrigated and nonirrigated fields of both provinces, which is common for soils with pH values above 6 [Curtin and Syers (1990), Ensminger (1954)]. Because adsorbed SO_4 is in kinetic equilibrium with that in solution (Chao, Harward, and Fang 1962), adsorption increases with increasing solution SO_4 concentrations. Conditions favoring leaching were not present at the time of fertilizer application in spring 1999 in Khorasan Province. Leaching might have been enhanced during this period in Golestan Province because of higher rainfall (>600 mm annually) compared to Khorasan Province (<400 mm annually). In irrigated fields of Khorasan Province, SO_4 adsorption was higher in treatments receiving no fertilizer S compared to those receiving 40 kg S ha^{-1}. It was also higher in the 0–30-cm depth compared to the 30–60-cm depth for irrigated fields.

Sulphate adsorption was low in all soils. However, the values were higher in the plots receiving no S compared to the plots receiving 40 kg S ha^{-1}. This may be due to a lower concentration of SO_4-S in the surface layer and a greater tendency for the soil colloids to adsorb SO_4-S compare to plots
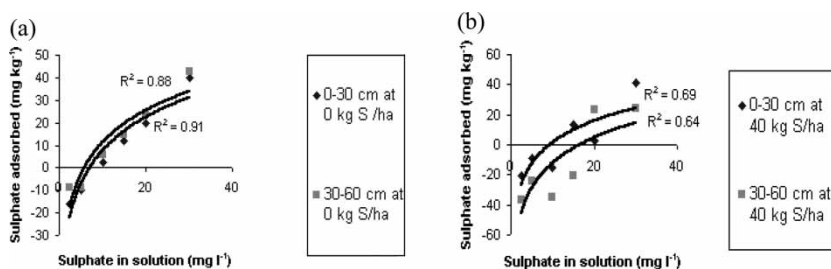

Figure 1. Sulphate adsorption in irrigated field of Golestan Province: (a) 0 kg S h^{-1} and (b) 40 kg S ha^{-1}.
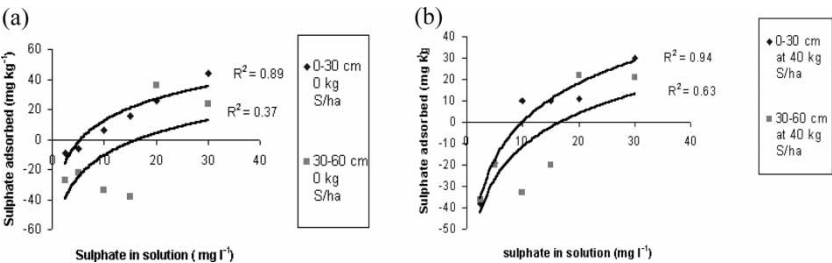
Figure 2. Sulphate adsorption in nonirrigated field of Golestan Province: (a) $0 \, kg \, S \, ha^{-1}$ and (b) $40 \, kg \, S \, ha^{-1}$.

that already received higher amounts of SO_4-S. This difference between the two depths may be partly explained by the fact that SO_4 is probably transported from the surface layer to the subsoil either by irrigation or by rainfall.

Values were almost similar for the two depths with $R^2 = 0.88^{**}$ for 0–30-cm depth and $R^2 = 0.91^{**}$ for 30–60 cm in irrigated field of Golestan Province (Figure 1). In nonirrigated fields, SO_4 adsorption was higher in plots receiving $0 \, kg \, S \, ha^{-1}$ compared to plots receiving $40 \, kg \, S \, ha^{-1}$. It was higher in the 0–30 cm depth ($R^2 = 0.69^*$ for 0–30 cm) compared with the 30–60 cm depth ($R^2 = 0.64^*$) (Figure 2). This difference between the two depths may be partly explained by the fact that SO_4 is probably transported from the surface layer to the subsoil either by irrigation or by rainfall. Therefore, there is a greater capacity to adsorb SO_4 in the surface layer in both irrigated and in unirrigated soils. More organic matter in the surface horizon may also induce greater adsorption of SO_4 by producing better physical and chemical properties and more microbial activity (Figure 3). Comparing soils from irrigated fields with soils from nonirrigated fields, the adsorption of SO_4 was higher in irrigated fields in both Golestan and Khorasan Provinces.

In Khorasan Province, SO_4-S adsorption was higher in soils from irrigated than rainfed fields (Figure 4). This might be related to better soil management
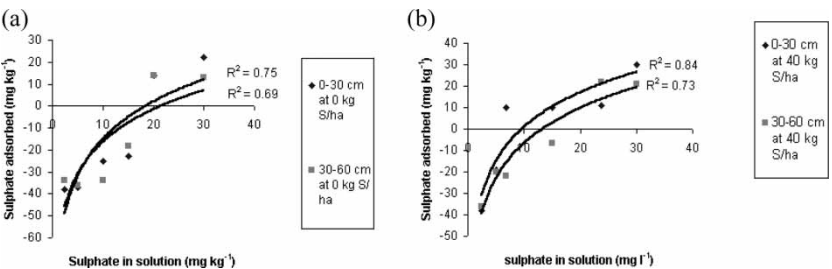

Figure 3. Sulphate adsorption in nonirrigated field of Khorasan Province: (a) $0 \, kg \, S \, ha^{-1}$ and (b) $40 \, kg \, S \, ha^{-1}$.
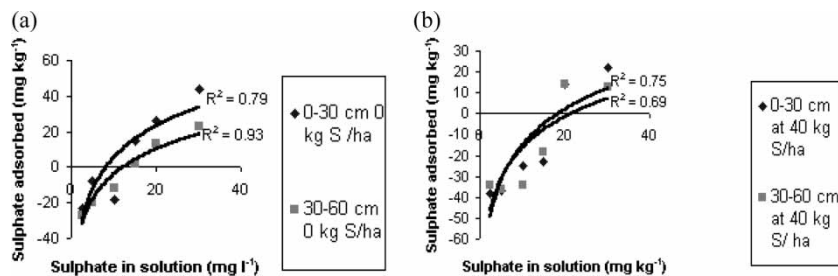
Figure 4. Sulphate adsorption in irrigated field of Khorasan Province: (a) 0 kg S ha^{-1} and (b) 40 kg S ha^{-1}.

practices accompanying irrigation, leading to improved physical, chemical, and biological conditions in the soil.

The SO_4-S adsorption capacity was low in both provinces, whereas the adsorption capacity of soils from irrigated fields was higher than those from rainfed fields, with larger adsorption in the surface zone compared to the subsoil. Also, adsorption was higher in the absence of applied S. This may be due to more vacant exchange sites in plots that received no S compared to plots that received 40 kg S ha^{-1} on sites that were able to adsorb SO_4-S.

Therefore, there is a greater capacity to adsorb SO_4 in the surface layer in both irrigated and in rainfed soils. More organic matter in the surface horizon may also induce greater adsorption of SO_4 by producing better physical and chemical properties and more microbial activity (Figure 4). Comparing soils from irrigated fields with soils from rainfed fields, the adsorption of SO_4 was higher in irrigated fields in both Golestan and Khorasan Provinces. The adsorption of Ca^{2+} and SO_4-S ions by variable-charge soils is higher when added in combination as a salt such as $CaSO_4$-$2H_2O$ (gypsum).

CONCLUSIONS

Results obtained with a wide range of soils lead to the conclusion that most Iranian soils with moderately high pH (more than 6) have little or no capacity to adsorb SO_4. This category would include most well-managed soils, so that in those satiations where demand for S is the highest, the capacity to retain added SO_4 against leaching may be small. Management practices, such as the application of lime or P, which reduce the affinity of the soil for SO_4, could have an adverse effect on S-supplying capacity by promoting leaching of SO_4 (Bolan et al. 1988). In addition, the low SO_4 retention characteristics of agricultural soils in Iran implies that fertilizers containing SO_4-S may not always be effective in correcting or preventing S deficiency in situations where leaching is important. Slow release of S, as provided by elemental S, may offer advantages in such situations.

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